

# Analysis of Acid-Leachable Barium, Copper, Iron, Lead, and Zinc Concentrations in Taylor Valley, Antarctic Stream Sediments

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By

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Approved by

A handwritten signature in black ink, reading "W. Berry Lyons". The signature is written in a cursive, flowing style. The "W" is large and prominent, followed by "Berry" and "Lyons". The signature is positioned above a horizontal line.

W. Berry Lyons, Project Advisor  
School of Earth Sciences

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## Abstract

The purpose of this study is to assess the concentrations of Barium (Ba), Copper (Cu), Iron (Fe), Lead (Pb), and Zinc (Zn) in sediment samples obtained from the Wales and Commonwealth streams located in Taylor Valley, Antarctica. These samples were collected at seven sample sites (three in Wales Glacier and four in Commonwealth Glacier) in 0 to 2 cm, 2 to 4 cm, 4 to 6 cm, and 6 to 8cm depth increments which resulted in 28 total samples. After the collection process, these samples underwent a volumetric 1:5 sediment: 10% HCl leach for 48 hours, filtration through 4- $\mu$ m pore-size, cellulose acetate membrane filters, and inductively coupled plasma mass spectrometry (ICP-MS) analyses in the Trace Element Research Laboratory at The Ohio State University. Upon completion of the analyses, results showed that the Wales samples had a higher average concentration of every metal element overall and at each depth increment when compared to the Commonwealth samples. In addition to the weak-acid leachate metal analyses, a second aliquot of one sediment profile from each stream was analyzed at Villanova University for the  $^{210}\text{Pb}$  activity via gamma spectroscopy. This was done to estimate the sedimentation rates at each of these sites. From the sedimentation rates, sedimentation fluxes were calculated for each element for each sediment profile at each of these sites. The data demonstrated that Fe is the most abundant element while Pb is the least abundant. Lastly, upon examination of results, it was found that the concentrations of these metals are often higher in samples collected closer to the surface. These findings suggest these streams, and their sources, have had little, if any, impact by anthropogenic input of metals, and that metal fluxes to the sediments are low.

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## Introduction

Antarctica has long been a place of interest for research as it is an extreme environment with strong winds, frigid temperatures, and rough terrain. Also, its ecosystem has been found to be one of the most fragile, as slight changes in albedo, nutrients, temperature, and precipitation can cause drastic change (Conovitz et al., 1998). To build upon this, the possibility of metals being added to the environment due to anthropogenic influences can also serve as a catalyst for said change.

To highlight the importance of assessing the metal concentrations and fluxes for this purpose, one can look to Martin and others' (1991) "Iron in Antarctic Waters", which discusses how iron is a limiting factor for productivity in the Southern Ocean and that the addition of iron would directly increase productivity. In connection with the scope of this present study, it is known that the Wales and Commonwealth are streams that empty into the Southern Ocean, and these streams are a potential source of bioavailable iron (Olund et. al. 2017). If there is an increased introduction of Fe to the Antarctica environment, one could infer that productivity in the ocean would increase.

The investigation of trace metals, especially lead concentrations within sediments, is a topic that has been widely studied. This is likely due to the fact that the global production of lead has steadily risen and is approximately 11.6 million tons per year (International Lead Association, 2018). Implications of this significant lead production are environmental disruption with perturbation of geochemical cycling pathways and negative effects to health (Ng & Patterson 1981). From Ng and Patterson's study, one can infer that if the levels of lead in the samples are above background concentration, the environment is receiving negative impacts as a result.

Lastly, this study analyzes not only Fe and Pb concentrations, but also Ba, Cu, and Zn. These heavy metals can also give indications of anthropogenic influence when compared to standardized concentration levels. Additionally, these heavy metals can cause the same detrimental effects as lead when introduced in large quantities.

## Site Description

### McMurdo Dry Valleys (MDVs)

The McMurdo Dry Valleys (76°30'-78°00'S, 160°00'-165°00'E) are 4500 km<sup>2</sup> of polar desert and make up the largest ice-free region of Antarctica (Levy, 2013). They are located within Southern Victoria Land and are just east of the Transantarctic Mountains, which prevent the advancement of East Antarctic Ice Sheet (EAIS) to the west (Chinn 1990). The environmental conditions of the MDVs are extreme due to strong katabatic winds and a precipitation average of around 100 mm/year (Doran et al., 2002). Also, for approximately the length of four months, the dry valleys experience continuous daylight and surface temperatures that range from -10 to 5°C during the austral summer. During the winter, the MDV experience 24-hour darkness and the temperatures can drop to between -40 to -8°C (Doran et al., 2002).

### Taylor Valley

The Taylor Valley (77°40'S, 162°52'E) is one of the McMurdo Dry Valleys and it is located between the Asgard Mountain Range and Kukri Hills. It is estimated to be 35 km long and 12 km wide (Fountain et al. 1999). Taylor Valley hosts 3 major, ice-covered lakes and more than 24 ephemeral streams (Fountain et al. 1999). The focus of this study is in the most eastern region of the valley where the Commonwealth and Wales streams are located.



**Figure 1:** Image of Taylor Valley, Antarctica obtained on December 8, 2013 by Landsat 8 satellite. (Nasa Earth Observatory, 2013)

## Ephemeral Streams

The ephemeral streams of the MDVs flow during late November to early January, for 4 to 10 weeks during the austral summer. The chief source of the water to the streams is the melting of nearby alpine glaciers, as groundwater, overland flow, and snowfall are not consequential contributors of water to the valleys (Chinn, 1993). These streams flow in permanent stream channels through unconsolidated alluvium and range from 1 km to 24 km in length (Gooseff et al., 2011). Minor fluctuations in temperature, albedo effect from snowfall, and sun position can lead to variations in amount of discharge. The flow of the stream has been noted to vary by as much as 5 to 10-fold in one day (Conovitz et al., 1998).

Commonwealth Stream is one of the two streams that are the focus of this study. In its western origins, the terrain is fairly flat, but to the east about 2 km, the stream steeply slopes down into buried ice that is likely the only minor source of water for Commonwealth (McKnight et al., 1999; Nylen et al., 2004). This buried ice is speculated to have been left by the advance of the West Antarctic Ice Sheet (WAIS) during the Late Glacial Maximum (Hall & Denton, 2000; Levy et al., 2013). About 3 km downstream, the geomorphology of Commonwealth Stream is observed to be a wide, braided delta. This stream flows into McMurdo Sound at New Harbor.



**Figure 2:** Image of Commonwealth Delta obtained by Dr. Chris Gardner during the 2019-2020 field season.





**Figure 3:** Image of Commonwealth Stream obtained by Dr. Chris Gardner during the 2019-2020 field season.

Wales Stream is the second area of interest in this study. It is south of and adjacent to Commonwealth stream. It varies in width but is measured to reach up to 130m wide. It begins its first 2 km in a steep and narrow valley but maintains a consistently mild slope thereafter. It also becomes a braided delta at its outlet and discharges into the South Ocean.



**Figure 4:** Image of Wales Delta obtained by Dr. Chris Gardner during the 2019-2020 field season.



**Figure 5:** Image of Wales Stream obtained by Dr. Chris Gardner during the 2019-2020 field season.

## Geology

The basement geology of the McMurdo Dry Valley floors consists of granitic dykes, amphyre, Paleozoic granite, and pre-Ordovician hornfels, schist, and marble metasediments. (Maurice et al., 2002). Permian Beacon sandstone then overlies this layer. Also, Jurassic Ferrar dolerite sills are found to slice through both of these layers. (Maurice et al., 2002).

The Taylor Valley soils largely consist of sand sized grains that are interbedded with cobble and boulder sized clasts. These clasts vary in composition, but generally consist of marble, gneiss, granite, sandstone, and dolerite (Doran et al., 1994). An accumulation of carbonate silt and clay from deltas are also common within the Taylor Valley. These deposits are thought to originate from older proglacial lakes (Doran et al., 1994). Also, several advances and retreats of the WAIS and EAIS are thought to be responsible for the till commonly found on the valley floor (Doran et al., 1994).

## Methods

### Sampling Methods

The stream sediment samples used in this study were collected in Taylor Valley during the month of January 2017 by Melisa A. Diaz and Kathy Welch from School of Earth Sciences, The Ohio State University. The sampling process began in the Wales Delta in a transect from South to North. Three sample sites were chosen for the Wales Delta and four samples were taken at each location. The four samples were taken in 2-centimeter depth increments with the first taken at 0-2 cm, followed by 2 to 4 cm, 4 to 6 cm, and 6 to 8 cm. A separate plastic scoop was used for each sample depth collection and it was rinsed with deionized water (DI) after each sample. The samples were then stored in individual, Whirl-Pak bags. Upon completion of sample collection in Wales Delta, the sampling process was repeated in Commonwealth Delta, but with 4 chosen sample sites that resulted in 16 samples. A new set of 4 plastic scoops were used for collection. Overall, there were 28 sample collected from Wales and Commonwealth stream beds. They were transported back to The Ohio State University and stored in a refrigerator until analysis in 2019.

### Leaching Methods

In May 2019, the sediment samples were oven-dried in aluminum weigh dishes at 80°C for 24 hours. Next, approximately six grams of each dried sediment sample were placed into thermoplastic weighing boats and weighed using a top-loading balance. A new weighing boat was used for each sample. After this step, the samples were put into individual, 50mL polyethylene Falcon tubes. Based on the mass of each sediment sample (approximately 6 grams), 30 g of 10% hydrochloric acid was added into each tube for a 1:5 sediment :10% HCl mass ratio. These samples were left to leach for 48 hours in a refrigerator at +4 °C. The sediment samples were then filtered using a 0.4- $\mu$ m pore-size, cellulose acetate membrane filter and put into another, new 50mL polyethylene Falcon tube. A new filter was also used for each sample and the filtration device was rinsed with our best deionized water (18 M $\Omega$ ) after every sample to avoid contamination.

### ICP-MS Methods

In preparation for ICP-MS analysis, two types of dilutions were made, 20x and 50x. The 20x dilutions contained 0.5mL sample, 0.2mL of reagent grade nitric acid (HNO<sub>3</sub>), and 9.3 mL of DI. The 50x dilution contained 0.2mL of the sample, 0.2mL of reagent grade HNO<sub>3</sub>, and 9.6 mL of DI water. For all dilutions, DI was added first to the individual, 15mL Falcon tubes by pipette. Reagent grade HNO<sub>3</sub> was then pipetted into the tubes within the fume hood. Following this step, the appropriate sample amount was then added to each tube under the fume hood with a new pipette tip for each sample. Finally, six standardized solutions were created and pipetted into individual 100 mL HDPE bottles. The table below details the concentrations of each standard in  $\mu$ g/L or ppb.

Element	Standard 4	Standard 3	Standard 2	Standard 1	Standard B	Standard A
Fe	25,000	10,000	1,000	500	250	50
Cu	50	20	2	1	0.5	0.1
Pb	20	8	0.8	0.4	0.2	0.04
Zn	10,000	4,000	400	200	100	20
Ba	10,000	4,000	400	200	100	20
In	10	10	10	10	10	10

**Table 1:** Concentrations of standards by element used for ICP-MS analyses.

Indium was used as an internal standard to monitor matrix effects when analyzing the samples. The equation  $C_1V_1=C_2V_2$  was used to calculate the needed concentration of indium for analyses. C1 represents the initial concentration, C2 represents the final concentration, V1 represents the initial volume, and V2 represents the final volume in the formula.

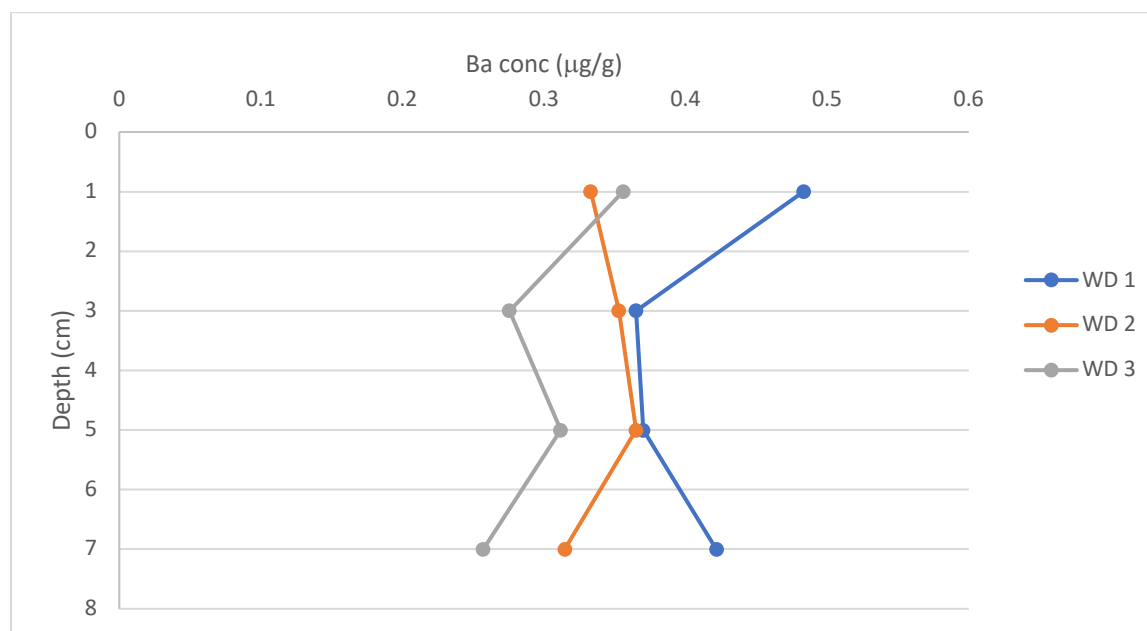
Regarding ICP-MS analyses, the ThermoFinnigan Element 2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was the instrument used. A sample queue was generated where the first 9 injections were 2% HNO<sub>3</sub> blanks and the 6 calibration standards. The leached samples were analyzed starting with injection 10. After every 10 samples, a duplicate sample, blank and STD 1 were run to monitor any instrument drift or matrix effects. Following the last sample, all 6 standards and 2 more blanks were analyzed. For each individual injection, the samples were analyzed 3 times and the average generated by the ThermoFinnigan software was used. Between samples, the system was rinsed with 2% HNO<sub>3</sub>.

## Results

The soils obtained from Wales and Commonwealth stream sediments were collected for the purpose of investigating metal concentrations. After completion of analyses, concentrations ( $\mu\text{g/g}$ ) of Ba, Pb, Fe, Cu, and Zn metals were plotted against soil depths (cm) for each sample. Samples collected at the same location were plotted within the same line (ex. WD 1 connects points of WD 1-1, WD 1-2, WD 1-3, and WD 1-4). The mid-depth of each sample was used to plot sample depth in all of the plots.

### Barium Concentrations

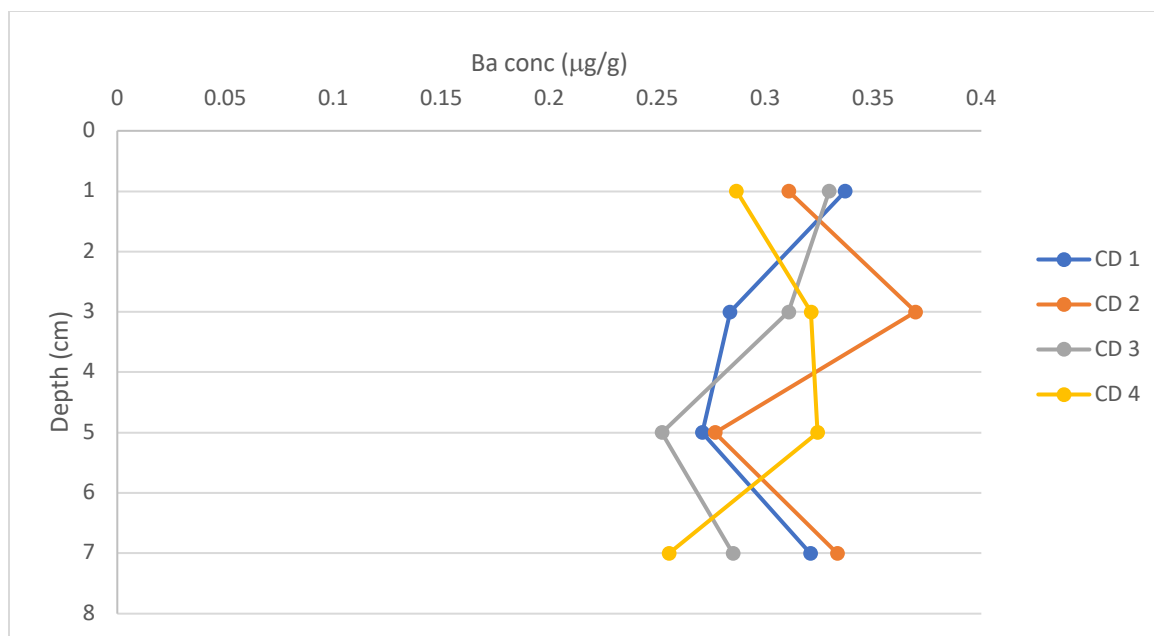
The concentrations of barium for the Wales sediment samples had a range of 0.257 to 0.483  $\mu\text{g/g}$ , a mean of 0.350  $\mu\text{g/g}$ , and a median of 0.354  $\mu\text{g/g}$  (Figure 6). Samples collected at the 0 to 2 cm depth were found to have the highest average Ba concentrations with a value of 0.391  $\mu\text{g/g}$  while samples collected at the 2 to 4 cm and 6 to 8 cm depth had the lowest average concentration at 0.331  $\mu\text{g/g}$ . Sample site 1 had the highest average concentration of Ba at 0.410  $\mu\text{g/g}$ , and sample site 3 had the lowest with a value of 0.300  $\mu\text{g/g}$ .



**Figure 6:** Acid-leachable barium concentrations in sediment samples from Wales Stream, Taylor Valley, Antarctica.

The concentration of barium for the Commonwealth sediment samples had a range of 0.252 to 0.370  $\mu\text{g/g}$ , a mean of 0.304  $\mu\text{g/g}$ , and a median of 0.311  $\mu\text{g/g}$ . Samples collected at the 2 to 4 cm depth were found to have the highest average Ba concentrations with a value of 0.321  $\mu\text{g/g}$  while samples collected at 6 to 8 cm depth had the lowest average concentration at 0.281  $\mu\text{g/g}$ . Sample site 2 had the highest average concentration of Ba at 0.323  $\mu\text{g/g}$ , and sample site 3 had the lowest with a value of 0.294  $\mu\text{g/g}$ .



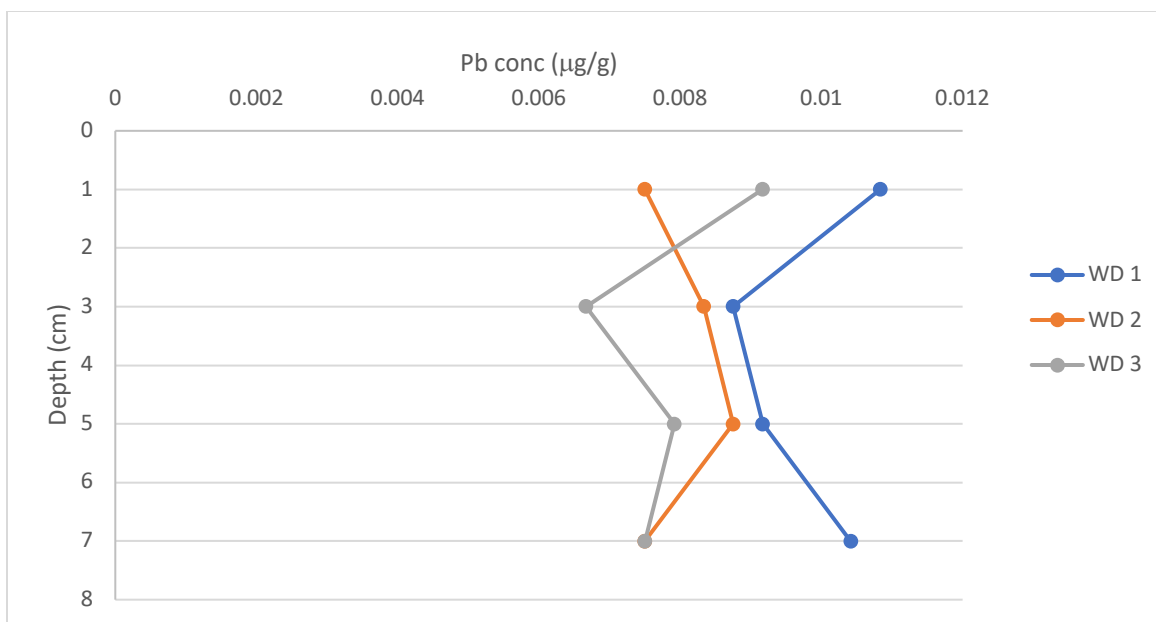


**Figure 7:** Acid-leachable barium concentrations in sediments samples from Commonwealth Stream, Taylor Valley, Antarctica.

Upon comparison of the values, the Wales samples had an overall higher average concentration of barium. Also, neither Commonwealth nor Wales had distinguishable patterns within sample depth concentrations.

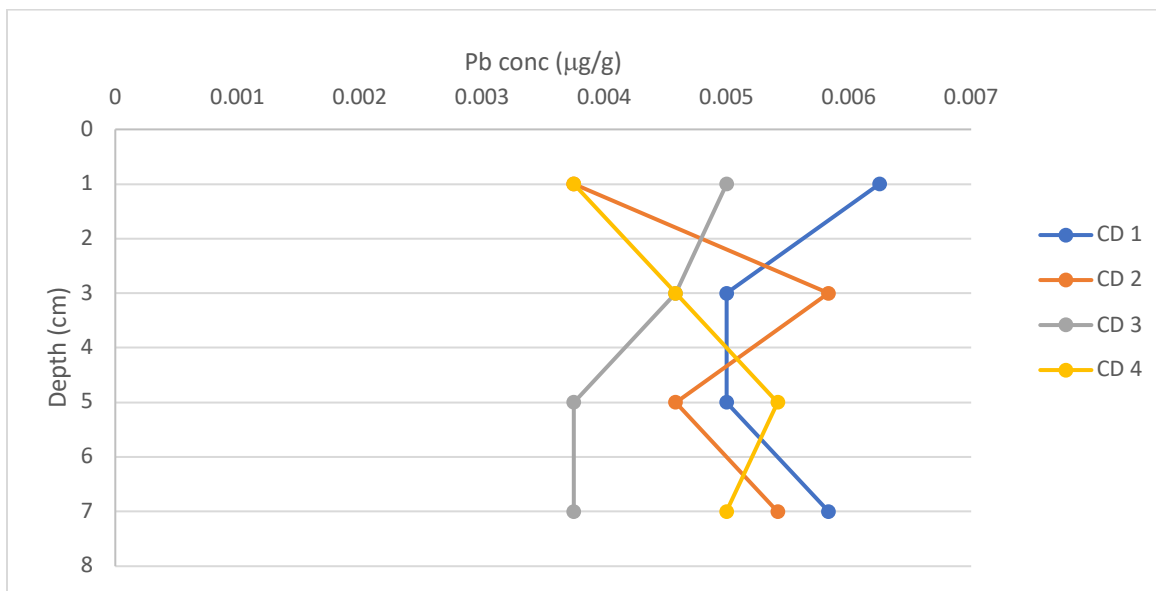
## Lead Concentrations

The concentration of lead for the Wales sediment samples had a range of 0.0067 to 0.0108  $\mu\text{g/g}$ , a mean of 0.0085  $\mu\text{g/g}$ , and a median of 0.0085  $\mu\text{g/g}$ . Samples collected at the 0 to 2 cm depth were found to have the highest average Pb concentrations with a value of 0.0092  $\mu\text{g/g}$  while samples collected at 2 to 4 cm depth had the lowest average concentration at 0.0080  $\mu\text{g/g}$ . Sample site 1 had the highest average concentration of Pb at 0.0098  $\mu\text{g/g}$ , and sample site 3 had the lowest with a value of 0.0078  $\mu\text{g/g}$ .



**Figure 8:** Acid-leachable lead concentrations in sediment samples from Wales Stream, Taylor Valley, Antarctica.

The concentration of lead in the Commonwealth sediment samples had a range of 0.0038 to 0.0063  $\mu\text{g/g}$ , a mean of 0.0048  $\mu\text{g/g}$ , and a median of 0.0050  $\mu\text{g/g}$ . Samples collected at the 2 to 4 cm and 6 to 8 depth were found to have the highest average Pb concentration with a value of 0.0050  $\mu\text{g/g}$  while samples collected at the 0 to 2 and 4 to 6 cm depth had the lowest average concentration at 0.0047  $\mu\text{g/g}$ . Sample site 1 had the highest average concentration of Pb at 0.0055  $\mu\text{g/g}$ , and sample site 3 had the lowest with a value of 0.0047  $\mu\text{g/g}$ .

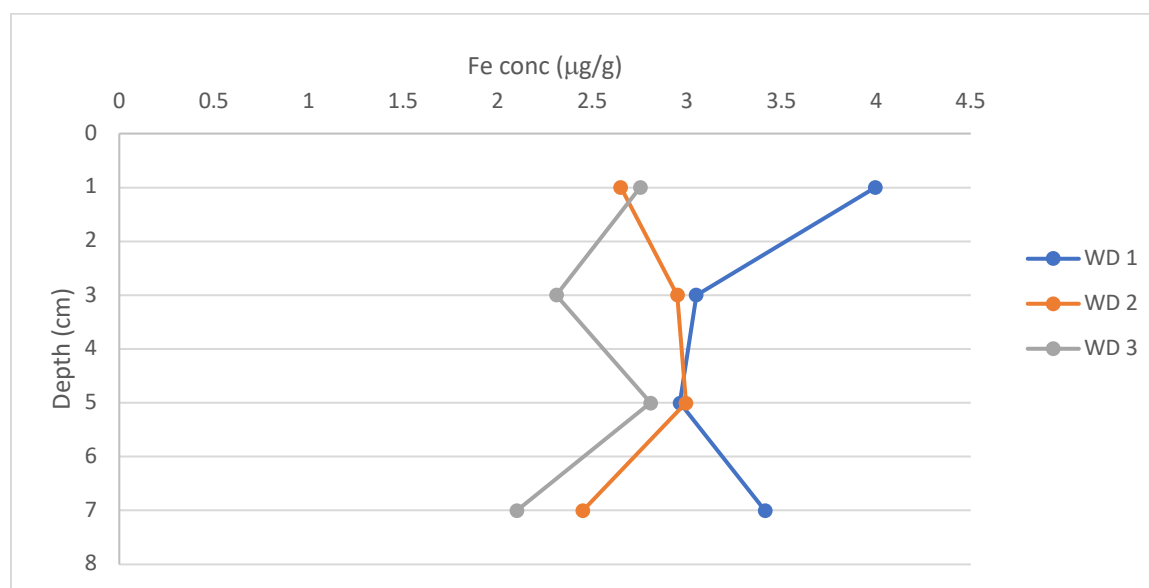


**Figure 9:** Acid-leachable lead concentrations in sediment samples from Commonwealth Stream, Taylor Valley, Antarctica.

Upon comparison, the Wales samples showed nearly double the average concentration of lead that Commonwealth samples had. Again, neither Commonwealth nor Wales had distinguishable patterns within sample depth concentrations.

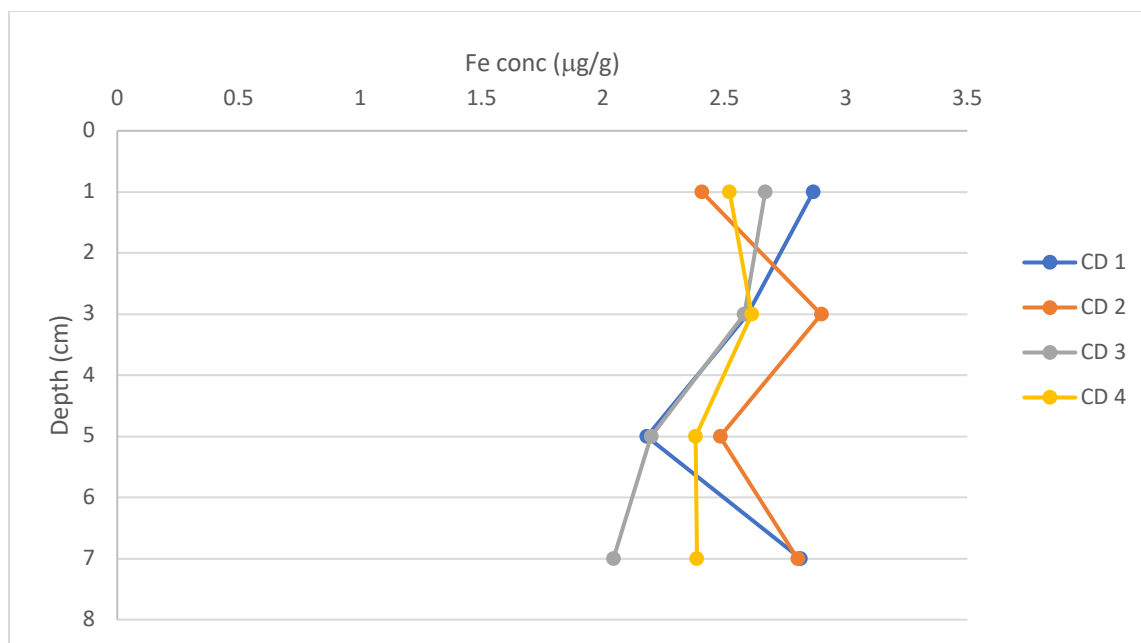
## Iron Concentrations

The concentration of iron for the Wales sediment samples had a range of 2.10 to 4.00  $\mu\text{g/g}$ , a mean of 2.87  $\mu\text{g/g}$ , and a median of 2.88  $\mu\text{g/g}$ . Samples collected at the 0 to 2 cm depth were found to have the highest average Fe concentration with a value of 3.13  $\mu\text{g/g}$  while samples collected at the 6 to 8 cm depth had the lowest average concentration at 2.66  $\mu\text{g/g}$ . Sample site 1 had the highest average concentration of Fe at 3.36  $\mu\text{g/g}$ , and sample site 3 had the lowest with a value of 2.49  $\mu\text{g/g}$ .



**Figure 10:** Acid-leachable iron concentrations in sediment samples from Wales Stream, Taylor Valley, Antarctica.

The concentration of iron in the Commonwealth sediment samples had a range of 1.90 to 2.90  $\mu\text{g/g}$ , a mean of 2.48  $\mu\text{g/g}$ , and a median of 2.53  $\mu\text{g/g}$ . Samples collected at the 2 to 4 cm depth were found to have the highest average Fe concentration with a value of 2.61  $\mu\text{g/g}$  while samples collected at the 4 to 6 cm depth had the lowest average concentration at 2.38  $\mu\text{g/g}$ . Sample site 2 had the highest average concentration of Fe at 2.65  $\mu\text{g/g}$ , and sample site 4 had the lowest with a value of 2.27  $\mu\text{g/g}$ .

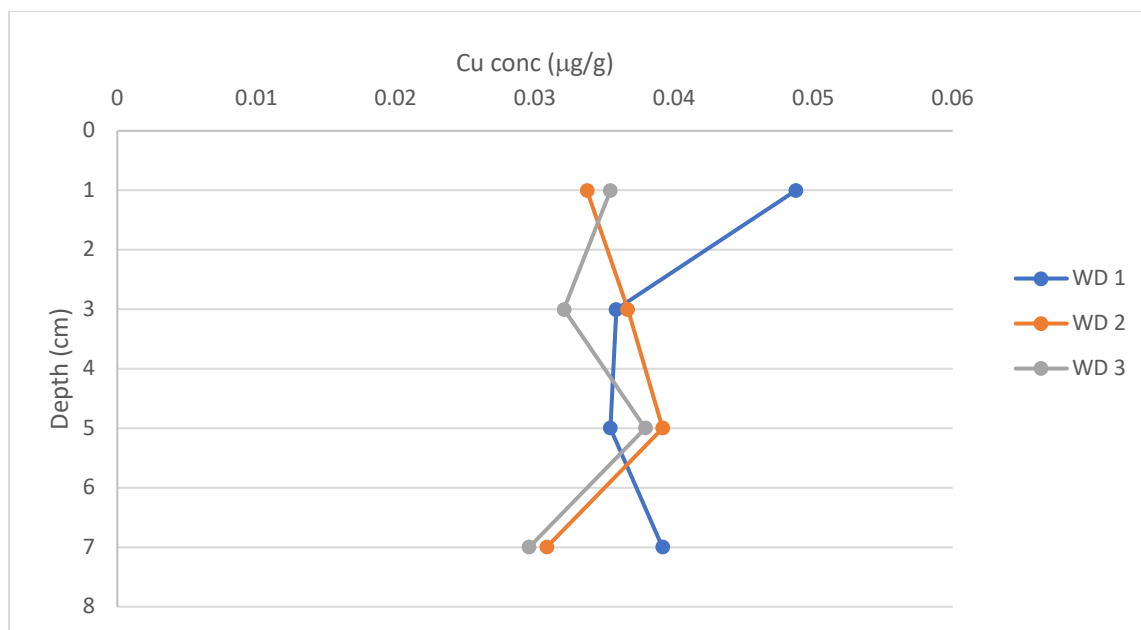


**Figure 11:** Acid-leachable iron concentrations in sediment samples from Commonwealth Stream, Taylor Valley, Antarctica.

Upon comparison, the Wales sample had the higher average concentration of iron. Neither Commonwealth nor Wales had distinguishable patterns within sample depth concentrations.

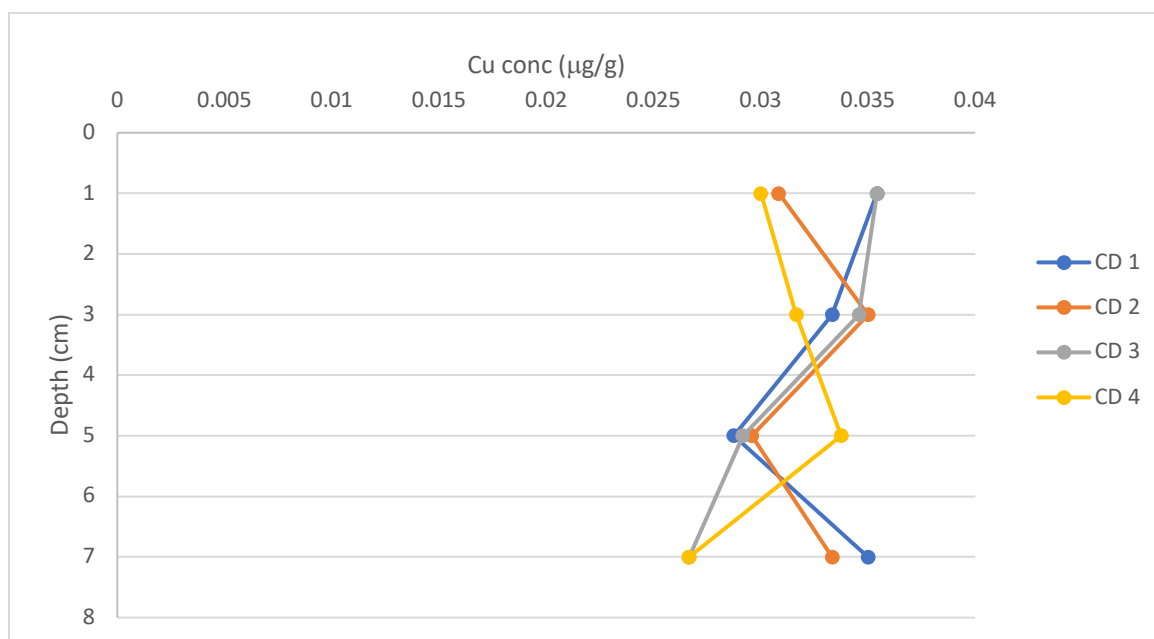
## Copper Concentrations

The concentration of copper for the Wales soil samples had a range of 0.0296 to 0.0488 µg/g, a mean of 0.0362 µg/g, and a median of 0.0356 µg/g. Samples collected at the 0 to 2 cm depth were found to have the highest average Cu concentration with a value of 0.0393 µg/g while samples collected at the 6 to 8 cm depth had the lowest average concentration at 0.0332 µg/g. Sample site 1 had the highest average concentration of Cu at 0.0398 µg/g, and sample site 3 had the lowest with a value of 0.0338 µg/g.



**Figure 12:** Acid-leachable copper concentrations in sediment samples from Wales Stream, Taylor Valley, Antarctica.

The concentration of copper for the Commonwealth soil samples had a range of 0.0288 to 0.0354  $\mu\text{g/g}$ , a mean of 0.0318  $\mu\text{g/g}$ , and a median of 0.0325  $\mu\text{g/g}$ . Samples collected at the 2 to 4 cm depth were found to have the highest average Cu concentration with a value of 0.0336  $\mu\text{g/g}$  while samples collected at the 4 to 6 cm depth had the lowest average concentration at 0.0303  $\mu\text{g/g}$ . Sample site 1 had the highest average concentration of Cu at 0.0331  $\mu\text{g/g}$ , and sample site 4 had the lowest with a value of 0.0305  $\mu\text{g/g}$ .

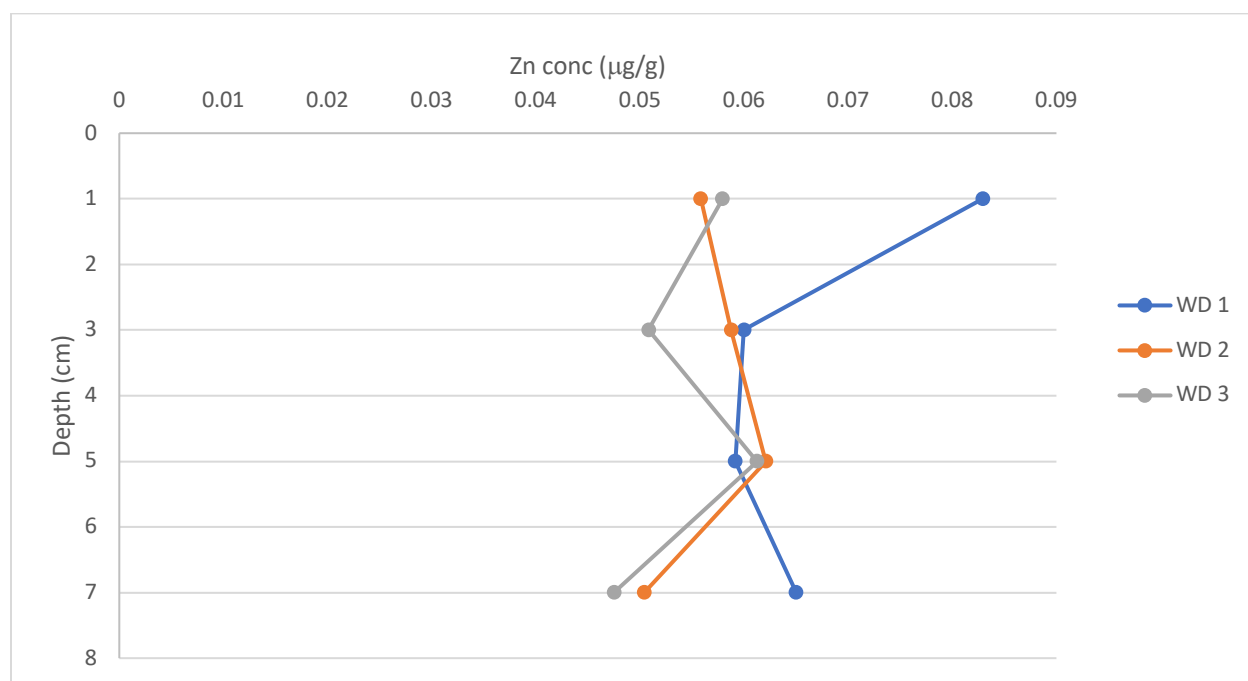


**Figure 13:** Acid-leachable copper concentrations in sediment samples from Commonwealth Stream, Taylor Valley, Antarctica.

Upon comparison, the Wales samples had the higher average concentration of copper. Both Commonwealth and Wales had no distinguishable patterns within sample depth concentrations.

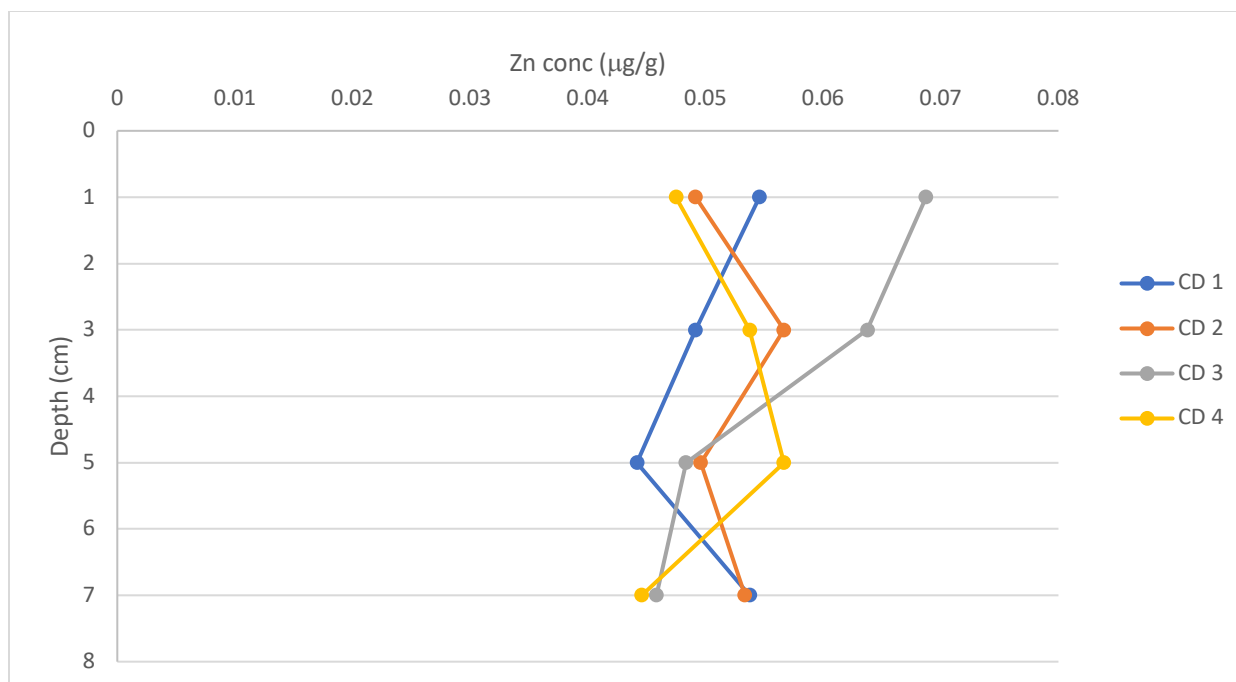
## Zinc Concentrations

The concentration of zinc for the Wales soil samples had a range of 0.0475 to 0.0829  $\mu\text{g/g}$ , a mean of 0.0593  $\mu\text{g/g}$ , and a median of 0.0590  $\mu\text{g/g}$ . Samples collected at the 0 to 2 cm depth were found to have the highest average Zn concentration with a value of 0.0656  $\mu\text{g/g}$  while samples collected at the 6 to 8 cm depth had the lowest average concentration at 0.0543  $\mu\text{g/g}$ . Sample site 1 had the highest average concentration of Zn at 0.066771  $\mu\text{g/g}$ , and sample site 3 had the lowest with a value of 0.0544  $\mu\text{g/g}$ .



**Figure 14:** Acid-leachable zinc concentrations in sediment samples from Wales Stream, Taylor Valley, Antarctica.

The concentration of zinc in the Commonwealth soil samples had a range of 0.0442 to 0.0688  $\mu\text{g/g}$ , a mean of 0.0525  $\mu\text{g/g}$ , and a median of 0.0515  $\mu\text{g/g}$ . Samples collected at the 4 to 6 cm depth were found to have the highest average Zn concentration with a value of 0.0558  $\mu\text{g/g}$  while samples collected at the 6 to 8 cm depth had the lowest average concentration at 0.0494  $\mu\text{g/g}$ . Sample site 3 had the highest average concentration of Zn at 0.0567  $\mu\text{g/g}$ , and sample site 1 had the lowest with a value of 0.0504  $\mu\text{g/g}$ .



**Figure 15:** Acid-leachable zinc concentrations in soil samples from Commonwealth Stream, Taylor Valley, Antarctica.

Upon comparison, the Wales samples had the higher average concentration of zinc. Neither Commonwealth nor Wales had distinguishable patterns within sample depth concentrations.

## Summary of Results

Overall, the Wales sediment samples had a higher average concentration of every metal when compared to Commonwealth's samples. Also, when comparing samples by average concentrations at each depth interval, Wales always had the higher values. Lastly, Fe was found to be the most abundant element while Pb was found to be the least abundant for both sites.

Wales sample sites, sample site 1 had the highest average concentration of every metal in the study while sample site 3 always had the lowest. At the sample depth of 0 to 2 cm, Wales was consistently shown to have the highest average metal concentrations. Samples of the 6 to 8 cm depth interval were commonly found to have the lowest average metal concentrations.

Lastly, upon analysis of the Commonwealth sample site data, sample site 1 had the highest average concentration of Pb, Cu, and Zn while sample site 2 had the highest concentration of Ba and Fe. Sample site 3 had the lowest average values of Ba, Pb, and Cu while sample site 4 had the lowest average values for Fe and Zn. At the sample depth of 2 to 4 cm, it was consistently shown that this depth interval had the highest average metal concentrations. Samples of the 4 to 6 cm depth interval were commonly found to have the lowest average metal concentrations for Pb, Fe, and Cu while the 6 to 8 depth interval had the lowest average values for Ba and Zn.

## Discussion

### Metal Concentrations

The weak acid-leachable trace metals concentrations in these Taylor Valley stream sediments are very low. Previous work throughout the world has observed much higher values in both lake and coastal marine sediments, ranging from 5.7 to 14.5  $\mu\text{g/g}$  for Pb, 1.3 to 4.4  $\mu\text{g/g}$  for Cu, 2.7 to 27.4  $\text{mg/g}$  for Fe, and 36.9 to 56.5  $\mu\text{g/g}$  for Zn. (Lyons and Fitzgerald 1980 & Lyons et al. 1983). It should be noted that these two prior studies did use a more corrosive leaching solution (1N  $\text{HNO}_3$  vs my 10%  $\text{HCl}$ ), and the concentration values of these two prior studies are still orders of magnitude higher than observed in the Antarctic stream sediments of the present study. These low values, as well as the comparison to previous work, strongly indicate very little to no anthropogenic input of metals to this Antarctic landscape. However, the Wales Stream sediments all show an increase in concentrations of Ba, Pb, Zn, Cu, and Fe toward the sediment-water interface. This type of concentration-depth profile is associated with an anthropogenic input of metal in modern times (Lyons and Fitzgerald 1980). Wales Stream enters the McMurdo Sound at New Harbor. New Harbor has a permanent camp that has been utilized by U.S. Antarctic Program scientists since the early 1960s. This camp is also associated with a helicopter landing area where people, equipment, and supplies are brought in. Therefore, this location has had active, human activities associated with it for some time. Because of all these things, even though the absolute concentrations of the weak acid-leachable metals are low, the profiles suggest that there has been a measurable increase in metal concentrations in close proximity to the camp in the recent past due to concentrated scientific activities there. Lastly, upon comparison to the relative concentrations of Ba (628  $\mu\text{g/g}$ ), Zn (67  $\mu\text{g/g}$ ), Cu (28  $\mu\text{g/g}$ ), and Pb (17  $\mu\text{g/g}$ ) in the upper continental crust in Rudnick and Gao (2003), it is found that the samples of this present study have much lower levels of every element.

### Metal Fractionation in Sediments

It is assumed that a 10%  $\text{HCl}$  leach solubilizes metals absorbed on mineral ion-exchange sites, associated with carbonate minerals and amorphous Fe and Mn oxides/hydroxides. In order to determine the partitioning of metals into the 10%  $\text{HCl}$  leachable fraction, I have compared the concentrations of Fe, Ba, Zn, Cu and Pb in this fraction to the total concentrations of these metals in sediment samples measured by XRF techniques by Dowling et al. (2019). These total concentrations are tabulated in Table 2. Also, Table 3 shows the percentage of the total concentrations of Ba, Cu, Fe, Pb, and Zn that were able to be acid-leached in Commonwealth samples on average. Each element had less than 1% of its total concentration acid leached. Dowling et al. (2019) analyzed one sample from Commonwealth Stream, but they have no data from Wales. The closest stream samples that they have to Wales Stream that drain from the south of Taylor Valley from the Kukri Hills is Von Guerand Stream (Table 2). The leachate data are orders of magnitude lower in concentration than the total values (Table 2), again supporting the idea that there is little anthropogenically introduced metal in these environments, as a higher percentage of the total would be acid-leachable if that was the case (Lyons and Fitzgerald, 1980). An important biogeochemical question is how mobile are these metals as the sediments are chemically weathered and physically transported, especially in this relatively pristine environment? In order to answer this question, I have normalized the metal concentrations using



both data sets to compare the leachates to the total, bulk sediment values. This is done by simply dividing all the other metal concentrations by the Pb values. Pb was chosen because it is one of the most particle-reactive elements and is not prone to dissolution, especially in oxidized environments. The normalized values in  $\mu\text{g/g}$  Fe: Ba: Zn: Cu: Pb for the Commonwealth sediment and the mean value for the Von Guerard Stream sediments are 3010:29:3.5:1:1 and 2270:44:3.3:0.9:1, respectively. The leachate values are 517:62:11:7.5:1 and 338:41:7:4.2:1, respectively for Commonwealth and Wales Streams. These data indicate the Fe is depleted, while Zn and Cu are enriched in the acid-leachable phase relative to the starting material, the bulk sediment in both streams. Ba is enriched in Commonwealth and essentially the same as the starting material in Wales. The depletion of Fe is not surprising, as like Pb, it is an insoluble element in oxidized settings. The data suggest that Cu and Zn are selectively incorporated into Fe-Mn oxides/hydroxides, which is a well-established geochemical concept (Little et. al 2014).

Stream Name	Ba	Cu	Fe	Pb	Zn
Commonwealth	529	19	54200	18	63
Von Guerand	667	17	49000	19	62
Von Guerand II.	870	12	31600	16	53

**Table 2:** Total Metal Concentrations of Stream Sediments in Taylor Valley, Antarctica in  $\mu\text{g/g}$  From Dowling et al. (2019)

Stream Name	Ba	Cu	Fe	Pb	Zn
Commonwealth	0.058	0.17	0.0046	0.027	0.083

**Table 3:** Percentage of the Total Metal Concentrations of Commonwealth That are Acid-Leached in This Study.

## Metal Fluxes

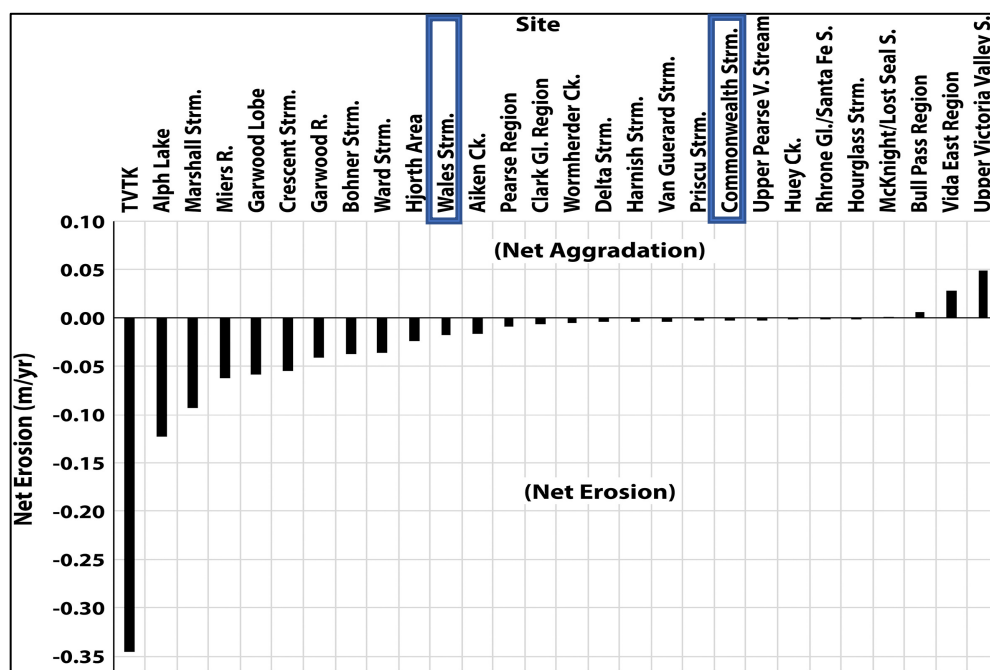
Dr. Steven Goldsmith at the University of Villanova determined  $^{210}\text{Pb}$  activities on a second aliquot of the samples using gamma spectroscopy. He did this for the purpose of estimating sedimentation rates at each site. He was successfully able to achieve one sediment profile for each stream bed. Sample site CD-4 was calculated to have a sedimentation rate of 0.73 cm/yr while sample site WD-2 was calculated to have a sedimentation rate of 0.15 cm/yr. These rates obtained by Dr. Goldsmith were then used to calculate sedimentation fluxes of Ba, Cu, Fe, Pb, and Zn at WD-2 and CD-4 sample sites with the formula : Sedimentation Flux  $\mu\text{g/cm}^2/\text{yr}$  = Sedimentation Rate (cm/yr) x Concentration of Element in 0-2 sample of site ( $\mu\text{g/g}$ ) x Density ( $2.7 \text{ g/cm}^3$ ) (See Table 4). The Commonwealth sample site was found to have a higher sedimentation flux of each element when compared to the Wales sample site.

Sample Site	Ba	Cu	Fe	Pb	Zn
WD-2	0.134	0.013	1.07	0.003	0.023
CD-4	0.565	0.059	4.22	0.007	0.094

**Table 4:** Sediment Fluxes of Ba, Cu, Fe, Pb, and Zn in  $\mu\text{g}/\text{cm}^2/\text{yr}$  for WD-2 and CD-4.

## Sedimentation vs. Erosion Rates

The sedimentation rates for the deltas of Commonwealth and Wales streams from this study were compared with the erosion rates of said streams from Levy et al. (2018). The erosion rate of Commonwealth stream was found to be approximately 0.5 cm/yr while Wales stream's erosion rate was found to be approximately 2.5 cm/yr (Figure 16). Wales Stream having a lower sedimentation rate than Commonwealth but having a higher erosion rate upstream reveals some characteristics of the geomorphology and flow of these streams. Firstly, as mentioned previously, Wales is narrow and steeply sloping in its first 2 km while Commonwealth begins fairly flat for the first few kilometers before it begins to slope. This difference in geomorphology upstream is likely the reason for the great difference in erosion between Commonwealth and Wales. Regarding the trend observed with a high erosion rate and low sedimentation rate of Wales, one can infer that the flow of Wales stream is strong enough to carry sediment far enough to be released into McMurdo Sound and not deposited in its braided delta. For Commonwealth, the possible reason for the lower erosion rate and higher sedimentation rate may be that more erosion occurs downstream when it travels more steeply through buried ice. Also, the greater deposition of sediments in Commonwealth occurring in the delta may be a result of a weaker flow that cannot carry the sediments to its outlet.



**Figure 16:** Analysis of Erosion/Sedimentation Rates in McMurdo Dry Valleys, Antarctica with specific focus on Wales and Commonwealth streams. Original graph obtained from Levy et. al (2018).

## Conclusions

- The analyses of acid-leachable metal elements from sediment samples collected in Wales and Commonwealth Streams, Taylor Valley, Antarctica revealed that Wales sediments have a higher concentration of barium, copper, iron, lead, and zinc overall and at every depth interval.
- Generally, samples collected closer to the surface had a higher concentration of metal elements when compared to values of samples from greater depths.
- A sedimentation rate of 0.73cm/yr was determined for the Commonwealth samples while Wales samples had a sedimentation rate of 0.15 cm/yr.
- These streams and their sources have had little, if any, impact by anthropogenic input of metals, and that metal fluxes to the sediments are low.

## **Recommendations for Future Work**

It would be useful to make a more detailed sediment profile for this locality. This could be done by taking more samples at smaller depth increments (e.g. centimeter and half centimeter intervals instead of 2-centimeter intervals). This would allow for better sedimentation rates to be calculated for the areas.

A second recommendation for future work is that more sedimentation rates are determined and for more locations. This study only has one sedimentation rate for each stream bed area. More sedimentation rates and locations would give more information about geomorphic change in the area.

Also, it would be useful to assess whether the metals are mobile by examine water samples from the streams.

Lastly, samples could be run in a SEM for spot-chemical analyses. This would aid in better assessment of there is anthropogenic influence.

## References Cited

- Barrett, J. E., Virginia, R. A., Wall, D. H., Cary, S. C., Adams, B. J., Hacker, A. L., & Aislabie, J. M. (2006) Co-variation in soil biodiversity and biogeochemistry in northern and southern Victoria Land, Antarctica. *Antarctic Science* 18, 535-548.
- Chinn, T.J. (1981) Hydrology and Climate in the Ross Sea Area. *Journal of the Royal Society of New Zealand* 11, 373-386.
- Chinn, T. J. (1993) Physical Hydrology of the Dry Valley Lakes. In *Physical and Biogeochemical Processes in Antarctic Lakes*, American Geophysical Union, 1-51
- Conovitz, P. A., McKnight, D. M., MacDonald, L. H., Fountain, A. G., & House, H. R. (1998) Hydrologic processes influencing streamflow variation in Fryxell basin, Antarctica. In *Ecosystem Dynamics in a Polar Desert: The McMurdo Dry Valleys, Antarctica* (ed. Priscu). American Geophysical Union, 93-108.
- Doran, P. T., McKay, C. P., Clow, G. D., Dana, G. L., Fountain, A. G., Nylen, T., & Lyons, W. B. (2002) Valley floor climate observations from the McMurdo Dry Valleys, Antarctica, 1986–2000. *Journal of Geophysical Research: Atmospheres* (1984–2012) 24, ACL-13.
- Dowling, C.B., Welch, S.A., Lyons, W.B. (2019) The geochemistry of glacial deposits in Taylor Valley, Antarctica: Comparison to upper continental crustal abundances. *Applied Geochemistry*, v.107, 91-104.
- Fountain, A. G., Lyons, W. B., Burkins, M. B., Dana, G. L., Doran, P. T., Lewis, K. J., McKnight, D.M., Moorhead, D.L., Parsons, A. N., Priscu, J.D., Wall, D. H., Wharton, R.A., and Virginia, R.A. (1999) Physical controls on the Taylor Valley ecosystem, Antarctica. *Bioscience* 12, 961- 971.
- Gooseff, M. N., McKnight, D. M., Doran, P., Fountain, A. G., & Lyons, W. B. (2011) Hydrological connectivity of the landscape of the McMurdo Dry Valleys, Antarctica. *Geography Compass* 9, 666-681.
- Hall, B. L. and Denton, G. H. (2000) Radiocarbon chronology of Ross Sea drift, eastern Taylor Valley, Antarctica; evidence for a grounded ice sheet in the Ross Sea at the last glacial maximum, *Geografiska Annaler. Series A: Physical Geography*, v. 82, 305– 336. doi: 10.1111/j.0435-3676.2000.00127.x.
- International Lead Association (2018). Lead Production & Statistics <https://www.ila-lead.org/lead-facts/lead-production--statistics>.
- Levy, J.S. (2013) How big are the McMurdo Dry Valleys? Estimating ice-free area using Landsat image data. *Antarctic Science* 1, 119-120.

- Levy, J.S., Fountain, A., Dickson, J., Head, J.W., Okal, M., Marchant, D.R., Watter, J. (2013) Accelerated thermokarst formation in the McMurdo Dry Valleys, Antarctica. *Nature. Sci Rep* 3, 2269. <https://doi.org/10.1038/srep02269>
- Levy, J.S., Fountain, A., Obryk, M.K., Telling, J., Glennie, C., Petterson, R., Gosseff, M., Van Horn, D.J. (2018) Decadal topographic change in the McMurdo Dry Valleys of Antarctica: Thermokarst subsidence, glacier thinning, and transfer of water storage from the cryosphere to the hydrosphere. *Geomorphology*. v. 323. 80–97
- Lyons, W.B., Fitzgerald, W.M. (1980) Trace Metal Fluxes to Nearshore Long Island Sound Sediments. *Marine Pollution Bulletin*. v.11-6. 157-161.
- Lyons, W.B., Armstrong, P.B., Gaudette, H.E. (1983) Trace Metal Concentrations and Fluxes in Bermuda Sediments. *Marine Pollution Bulletin*. V.14-2. 65-68
- Little, S.H., Sherman, D.M., Vance, D., and Hein, J.R.. (2014) Molecular controls on Cu and Zn isotopic fractionation in Fe–Mn crusts. *Earth and Planetary Science Letters*. V.396. 213-222. <https://doi.org/10.1016/j.epsl.2014.04.021>
- Maurice, P. A., McKnight, D. M., Leff, L., Fulghum, J. E., & Gooseff, M. (2002) Direct observations of aluminosilicate weathering in the hyporheic zone of an Antarctic dry valley stream. *Geochim. Cosmochim. Acta* 66, 1335-1347.
- Martin, J. H., Gordon, R. M. and Fitzwater, S. E. (1990) Iron in Antarctic waters, *Nature*, v. 345, 156–158. doi: 10.1038/345156a0.
- McKnight, D. M., Niyogi, D. K., Alger, A. S., Bomblies, A., Conovitz, P. A., & Tate, C. M. (1999) Dry Valley streams in Antarctica: Ecosystems waiting for water. *Bioscience* 12, 985- 995
- Ng, A., Patterson, C.C. (1982) Changes of lead and barium with time in California off-shore basin sediments. *Geochim. Cosmochim Acta* v.46-1, 2307-2321.
- Nylen, T. H., Fountain, A. G. and Doran, P. T. (2004) ‘Climatology of katabatic winds in the McMurdo dry valleys, southern Victoria Land, Antarctica’, *Journal of Geophysical Research*, v. 109, D03114. doi: 10.1029/2003jd003937.
- Olund, S., Lyons, W.B, Welch, S.A., Welch, K.A. (2018) Fe and Nutrients in Coastal Antarctic Streams: Implications for Primary Production in the Ross Sea. *Journal of Geophysical Research*. v.123-12, 3507-3522. <https://doi.org/10.1029/2017JG004352>